All About ZIRCONIA

A primer on what it is, how to use it and which one goes where

by Dr. John O. Burgess

Dr. John O. Burgess received his dental degree from Emory University School of Dentistry, completing a one-year GPD and a two-year general dentistry program. An adjunct professor at the University of Alabama at Birmingham School of Dentistry, he has authored or co-authored more than 400 manuscripts and given more than 1,000 all-day CE programs nationally and internationally.

Burgess is a member of the Restorative Academy, the Operative Academy, the Academy of Esthetic Dentistry and the American and International Associations for Dental Research, and has served on the Council of Scientific Affairs for the ADA. He is active in clinical trials examining the effectiveness of ceramic materials, adhesives, bulk-cured composite and bioactive materials. Burgess would like to thank Ivoclar Vivadent and Dr. Tom Hill for their assistance with this article.
Introduction

A 2015 survey reported that the most-prescribed ceramic material for posterior crowns was monolithic zirconia, with lithium disilicate most often prescribed for anterior crowns. This increase in prescribing full-contour zirconia as the favored posterior ceramic material is due to several factors:

- An increased demand for aesthetic restorations.
- The increased cost of metal (gold $1,340/ounce).
- Zirconia being a strong aesthetic material.
- The development of CAD/CAM systems.

Zirconia was introduced as a framework for dental restorations, which was veneered with feldspathic porcelain. At the time of its introduction, few computer-aided design and computer-aided manufacturing (CAD/CAM) systems were available to fabricate milled zirconia restorations.

With the development of newer, more accurate CAD/CAM systems, milling zirconia restorations became commonplace. The introduction of zirconia was a perfect fit with the improved CAD/CAM systems, producing relatively inexpensive aesthetic restorations with improved mechanical properties.

Zirconia has evolved through several significant modifications, and clinicians must be aware of the properties and differences between zirconia materials because these factors affect the success or failure of the final restoration.

What is dental zirconia?

Zirconium is a soft silver-colored metal found as a mineral called zircon (ZrSiO₄). It is mined primarily from large deposits in Australia and Africa and shipped to processing plants such as Tosoh (Japan), the largest producer of refined zirconia powder. Zircon is purified and during the production process metal oxides are added: yttrium to stabilize the polycrystals; aluminum to prevent water corrosion; hafnium oxide to reduce pore development; and other coloring components to produce a powder that is pressed into a disk or block and partially sintered.

The partially sintered zirconia is milled into a framework or restoration, then further sintered, which produces approximately 20 percent shrinkage in the finished restoration. The density of zirconia is recorded on each block or puck, because density determines the shrinkage during sintering. The mill enlarges the final restoration to compensate for the shrinkage during sintering.

Zirconia is a polymorphic material that may exist in three crystallographic forms, depending on temperature and pressure: monoclinic (stable at room temperature up to 1,170°C), tetragonal (stable at 1,170–2,370°C), and cubic (stable from over 2,370°C to its melting point, 2,716°C). At room temperature, pure zirconia is present in the most stable phase, monoclinic. As the temperature rises to about 1,170°C, the monoclinic phase transforms into the tetragonal phase, accompanied by a shrinkage in volume of approximately 4–5 percent. The tetragonal phase converts into the cubic phase at about 2,370°C, with only minimal changes in volume.²⁻³
Dental zirconium dioxide is formed into a polycrystalline ceramic called yttrium-stabilized tetragonal zirconia polycrystals, or simply “zirconia.” Materials containing only tetragonal phase are strongest, while cubic-containing zirconia is significantly weaker but more translucent (cubic zirconia). The yttrium oxide, or yttria, content largely defines the mechanical and physical properties:

- Zirconia containing 3 mole-percent yttria is strongest (100 percent tetragonal phase) but most opaque.
- Zirconia containing 5 mole-percent yttria produces a more translucent material, with approximately 50 percent cubic phase.

Yttrium increases the zirconia grain size and lowers the coefficient of thermal expansion.

Ceramic flexural strength vs. fracture toughness

Flexural strength specimens are polished or milled samples (2 by 4 by 22 millimeters) and the strength is affected by the surface roughness of the specimen. Fracture toughness describes the ability of a material to resist crack propagation or how a crack spreads from a notched specimen. Cracks originate from flaws in materials—created by finishing, machining or porosity—and act as an initiation point for crack growth. For example, a car windshield hit with a rock chips the windshield, and the crack spreads from the chipped area across the windshield.

The energy required to grow the crack is measured by fracture toughness. Low toughness can lead to chipping and bulk fracture in materials. Fracture toughness measurements for feldspathic porcelain range from 1 to 1.3, translucent zirconia, 2–4, and opaque zirconia ranges from 7–9 MPa•m$^{1/2}$. Chipping occurs more frequently in the less-tough veneering materials compared with the zirconia frame. 5Y-TZP containing more than 50 percent cubic phase has little or no low temperature degradation and lower fracture toughness, and because the material has little residual stress, water corrosion is limited. High-cubic-containing zirconia is weaker but its strength does not degrade further from low-temperature degradation.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>High mechanical properties</td>
<td>High mechanical properties</td>
<td>Lower mechanical properties</td>
</tr>
<tr>
<td>White opaque</td>
<td>Some translucency</td>
<td>High translucency</td>
</tr>
<tr>
<td>Low temp degradation</td>
<td>Decreased low temperature degradation</td>
<td>Little or no low temperature degradation</td>
</tr>
<tr>
<td>Mainly tetragonal phase</td>
<td>Tetragonal and cubic phases</td>
<td>&gt;Cubic less tetragonal phases</td>
</tr>
</tbody>
</table>

Table 1: Defining zirconia used in dentistry by the yttrium content and its effect on physical and mechanical properties.
Zirconia evolves

Until 2014, zirconia contained 3 mole-percent yttria, or approximately 5 weight-percent. The original frame or opaque zirconia materials (Lava, BruxZir, Cercon, IPS E.max ZirCad, DC-Zirkon) were composed of yttria partially stabilized tetragonal polycrystals larger than 1 micron (1µ) with a small cubic component. Partially stabilized tetragonal crystals spontaneously revert to the monoclinic crystal with a 3–5 percent expansion by low-temperature transformation. Low-temperature transformation to the monoclinic phase begins at the restoration surface and produces a rougher occluding surface. The fear was, because zirconia was three times harder than the occluding enamel, that opposing enamel wear would increase, and continue to increase as the restoration aged and the zirconia continued to transform. To reduce this potential wear and reduce the opacity of the restoration, the zirconia frame was covered with veneering porcelain. Unfortunately the veneering material was porcelain with low flexural strength and fracture toughness, creating chipping of the veneered restoration.

After 2014, the zirconia crystal size decreased to approximately 0.2–0.5µ and increased yttria was added to stabilize zirconia by forming the cubic phase, which decreased low-temperature degradation. With these changes the veneering material was eliminated; as long as the tetragonal form was present, the positive effect—transformation toughening—created a transformation zone around forming cracks that slowed crack growth, producing few chips and fractures in the frame material.

An accelerated aging test for measuring transformation from tetragonal to monoclinic phase is conducted by autoclaving the specimens under steam pressure. This in vitro test demonstrates that grain size affects transformation and, within limits, small grains transform more slowly. An hour of autoclaving represents approximately 3–5 years of intraoral function. X-ray diffraction of aged tetragonal containing zirconia, translucent-containing zirconia and cubic-containing zirconia demonstrates reduced low-temperature transformation to monoclinic phase in cubic-containing zirconia.

Recently the tetragonal-to-monoclinic transformation was tested by measuring the change of partially stabilized (tetragonal-containing) zirconia crowns (Lava Plus from 3M) cemented in vivo and worn for 12–14 months (Fig. 1). After that period the crowns were removed and transformation was measured using X-ray diffraction (Fig. 2). The monoclinic transformation was 10.6 percent—a small change.

Opaque (3 mole-percent yttria) dental zirconia has high fracture toughness (5–9 MPa·m^{1/2}), with a flexural strength...
of 1,000–1,400 MPa. The original frame zirconia contained 3 mole-percent yttria to partially stabilize the tetragonal phase. Alumina (0.025 percent) was added to stabilize grain boundaries, to act as a sintering aid to decrease pore formation during sintering of the green state zirconia, and to prevent water corrosion. But the alumina produced additional opacity in the final restorations (Fig. 3, p. 68). Water corrosion affects all ceramic materials and leads to decreased strength with water or saliva storage.

The second major change in zirconia produced a more aesthetic translucent zirconia by reducing alumina from 0.25 weight-percent to 0.05 weight-percent while maintaining the same yttria component as the original opaque frame material. Although the reduction in alumina content produced a more aesthetic restorative material, zirconia was still too opaque for anterior restorations. The most recent version of zirconia (translucent) alumina remained at 0.05 weight-percent while yttria increased from 3 mole-percent to 5–8 mole-percent, depending upon the brand. At 5–8 mole percent yttria, the zirconia contains more cubic phase, preventing low-temperature degradation and improving zirconia translucency (Fig. 4).

Cubic-containing zirconia is more translucent but has lower mechanical properties. Translucent zirconia containing 4 or 5 mole-percent yttrium has a flexural strength of 600–900 MPa and a fracture toughness of 2.2–4 MPa•m$^{1/2}$, compared with opaque 3 mole-percent yttrium-containing zirconia's flexural strength of 1,000–1,400 MPa and fracture toughness of 5–9 MPa•m$^{1/2}$. Lower fracture toughness of translucent zirconia materials could mean more chipping and cracks in the translucent zirconia material.

Translucent zirconia has similar but higher flexural strength and fracture toughness compared with IPS E.max lithium disilicate, and this material could be considered a stronger but less translucent lithium disilicate. Translucent zirconia contains approximately 50 percent cubic crystals, which are weaker and do not transform. Zirconia with 8 mole-percent yttria will completely stabilize the cubic phase, whereas the third generation of zirconia with 5 mole-percent yttria is partially stabilized zirconia with approximately 50 percent cubic zirconia.

Stabilized cubic zirconia does not transform at room temperature, and therefore cubic zirconia will not undergo transformation toughening or low-temperature degradation. Translucent zirconia has lower mechanical properties but does not transform over time.

Current zirconia can be classified into two basic groups:
• Strong 3 mole-percent Y-TZP (fully tetragonal): IPS E.max ZirCad LT and MO, Lava Plus, BruxZir, Katana HT.
• Cubic phase-containing, more translucent 4–5 mole-percent Y-TZP (with reduced mechanical properties): IPS E.max ZirCad MT Multi and MT, BruxZir Ant, Lava Esthetic, Katana UTML.

Wear of zirconia and the opposing enamel

Multiple in vitro and in vivo studies have reported the low wear of zirconia-opposing enamel.12–17 Despite the lower strength and fracture toughness of translucent zirconia, no surface fracturing or roughening was observed during our wear testing, which used a unground enamel cusp and a 2mm slide across the ceramic being tested (Fig. 5).
Zirconia specimens after wear testing remained smooth throughout the wear process, and limited opposing enamel wear was seen. In our laboratory, wear has been reported in multiple studies comparing wear of the opposing enamel vs. zirconia, and the following can be summarized from the results:

- Polished zirconia wears the opposing enamel 10 times less than feldspathic porcelain (the ceramic covering porcelain fused to metal restorations).
- Polished zirconia wears the opposing enamel slightly less than Type IV gold-opposing enamel.
- Wear does not increase with time nor autoclaving (an accelerated aging test to induce low-temperature transformation).
- Wear of glazed zirconia was significantly greater to the opposing enamel compared with polished, nonglazed zirconia.
- The articulating surface opposing enamel should be polished zirconia in all anterior and especially posterior areas.

Lack of opposing enamel wear and higher fracture toughness of zirconia has led to an effective posterior restorative material recommended for patients with bruxism and longer-span fixed partial dentures.

**Why is dental zirconia opaque? How is it different from cubic zirconia?**

Why does a curing light not penetrate zirconia? When the properties of a material are the same in all directions, the material is isotropic. For polycrystalline materials like zirconia, the grain orientations are random and have different refraction indexes (Fig. 6). The tetragonal phase of zirconia is nonuniform in a three-dimensional space; therefore, light has preferred directions when passing through a tetragonal grain of zirconia. If light passes through one tetragonal grain and then hits another tetragonal grain with a different preferred direction at its grain boundary, the light will scatter.

Cubic zirconia, on the other hand, is isotropic. When light hits the grain boundary of two grains of cubic zirconia, it is more likely that they will share preferred directions and allow the light to pass through. Birefringence is the optical property of a material having a refractive index that depends on the polarization and propagation of light. Optically anisotropic materials are birefringent. See the path light takes in attempting to pass through zirconia (Fig. 6).

Light transmission has important implications when light-curing zirconia
A zirconia thickness of 0.5mm shows a 50 percent decrease in light transmission and a 75 percent reduction at 1mm thickness. With moderate staining and 0.5mm thickness, light transmission is reduced by 85 percent; at 1mm there is a 95 percent reduction.18,19

Some translucent zirconia has colorants added internally to improve the chroma of the zirconia and to reduce laboratory processing time. The optimal balance between translucency and strength continues to be modified to develop an optimal balance for an aesthetic strong restoration.

Opaque zirconia may be beneficial in some cases, especially when masking a single discolored tooth. Translucent zirconia is less translucent than lithium disilicate or enamel; if a highly translucent anterior restoration is needed, E.max or layering the facial surface of the zirconia restoration is a possible solution. The improved translucent zirconia makes it a more viable option for less demanding monolithic anterior restorations than previous versions of zirconia.

Zirconia is supplied in disks, multilayered disks and machinable blocks. First introduced by Kuraray, the multilayered disk is now supplied in blocks that can be sintered in ovens with a 30-minute sintering cycle, making chairside zirconia milling a clinical reality. Ivoclar has introduced IPS E.max ZirCad MT Multi when high mechanical strength, low wall thicknesses and high aesthetics are needed. Suitable for monolithic and veneered crowns and bridges for the anterior and posterior regions, its flexural strength ranges between 850 and 1,200 MPa.

**Bonding or cementing a zirconia restoration**

Bonding a monolithic zirconia restoration is necessary when the preparation is short or overtapered, or when the restoration lacks the desired thickness (generally 1mm reduction on the occlusal of the prepared tooth). Because thin occlusal restorations may fracture, bonding the restoration is strongly recommended.20 We measured the fracture strength of sandblasting the intaglio surface of zirconia crowns and bonding them with RelyX Unicem 2 or cementing with a resin-modified glass ionomer (RelyX from 3M). The fracture strength of the cubic-containing crowns was maintained when bonded but not cemented. Bonding strengthens thin zirconia crowns.

There are three types of dual-cured resin cements:

- **Total-etch (most retentive):**
  - Variolink Esthetic from Ivoclar,
  - Calibra from Dentsply.
- **Self-etching (intermediate retention):** Panavia V5, Kuraray.
- **Self-adhesive (less retentive):**
  - Unicem2, SpeedCem Plus.

Nonamine dual-cured resin cements have been developed with excellent color stability; Variolink Esthetic and Panavia V5 are good color-stable resin cements. Both have new initiators and no longer use an amine system. Total-etch cements require etching the prepared tooth with phosphoric acid, applying a bonding agent to the tooth and ceramic, and applying a dual-cured resin cement. While total-etch cements produce the greatest retention, light-curing the adhesive creates a film and may interfere with seating the restoration. Bonding is indicated with short, tapered preparations, with long-span FPDs and with thin restorations. Bonding is not always required.

It is difficult to bond to the restoration at times because of poor isolation and possible contamination of the bonding agents. In these cases, cementing with resin-modified glass ionomer requires less time (reducing contamination) and provides a successful cementation. RMGIs have easier cement removal after set and have a successful clinical record.
The clean-prime-cement (CPC) bonding technique

Bonding to zirconia provides predictable long-term bonds22–29 if the sequence below is followed every time.

After a restoration is tried in, phosphate groups from phospholipids in saliva occupy the bonding sites on the zirconia restoration and block the 10MDP monomer. Trying to bond to this surface is like trying to park two cars in the same parking space; both cars (adhesives) can’t occupy the bonding space. To deal with contamination, these procedures are recommended:

1. **Clean the prepared tooth** with fine pumice and water to remove any remaining provisional cement.

2. **Clean the intaglio surface** of contaminated zirconia restoration by sandblasting with alumina using Etch Master (Groman) or a Microetcher (Danville Engineering) and 30–50u alumina, 30psi for 10 seconds. Saliva-produced phosphate groups can’t be removed with phosphoric acid or alcohol, but Ivoclean (Ivoclar), a saturated solution of zirconia, effectively decontaminates the zirconia. Sodium hypochlorite has been recommended21 but our testing shows that applying sodium hypochlorite to zirconia reduces the zirconia-to-tooth bond if the hypochlorite contaminates dentin.

3. **Prime the clean intaglio surface** by applying Monobond Plus (Ivoclar), a 10MDP-containing primer; Z Prime (Bisco) or a 10MDP-containing adhesive (Scotchbond Universal, 3M).21–28 Monobond Plus or the Kuraray Ceramic Primer have silane and a phosphate monomer to bond to zirconia. Silane-containing phosphate bonding systems can be used for lithium disilicate or zirconia, so one material can simplify your procedures.

4. **Bond.** The two cements easiest to use in this situation are Panavia V5 (Kuraray) or RelyX Ultimate (3M), because no light-curing of the primer or adhesive is necessary with either. Using a contact cement, the bond forms when the resin cement contacts the adhesive or primer, preventing an adhesive film buildup that could prevent restoration seating. Our testing showed that you can bond to zirconia and the zirconia bond is the same as bonding to lithium disilicate at 24 hours and after 5-month water storage and 10,000 thermocycles.

All groups (lithium disilicate and zirconia) showed a reduction in bond after water storage. Clinical implications of this bond durability are important for conservative partial coverage zirconia restorations, resin-bonded fixed partial dentures, onlays and veneers.

References:


12. Lawson N et al. Wear of enamel opposing zirconia and lithium disilicate after adjustment, polishing and glazing.